NASI. 60: 1247

JUN 16 1978

NASA Technical Paper 1247

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JUNE 1978

NASA

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NASA TM 80.1247

NASA Technical Paper 1247

Catalytic Decomposition of Methanol for Onboard Hydrogen Generation

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**Scientific and Technical
Information Office**

1978

CATALYTIC DECOMPOSITION OF METHANOL FOR ONBOARD HYDROGEN GENERATION

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SUMMARY

The steam reformation of an equimolar mixture of methanol and water on a copper chromite catalyst was studied at three furnace temperatures and at methanol space velocities from 800 to 2600 per hour. The hydrogen space velocity could be related to the reactor temperature by the equation $Sv = A \exp(-\omega/T)$, where A and ω are constants determined for each value of α and T is temperature. At a methanol conversion of 0.87 and a reactor temperature of 589 K, the extrapolated value of the hydrogen space velocity was 9400 per hour. This velocity was used to estimate the size of an onboard hydrogen reactor for automotive applications. Such a reactor would need only about 0.8 liter of catalyst to produce 7630 STP liters (1.5 lb) of hydrogen per hour. This quantity of catalyst would fit into nine tubes 17.8 centimeters long and 2.54 centimeters in inside diameter, which is smaller than most mufflers. The reactor products would contain 12 to 13 percent more chemical energy than the incoming methanol and water.

INTRODUCTION

Recently, hydrogen has been receiving much attention as a fuel or fuel additive for internal combustion engines. The major problems associated with hydrogen as a fuel are onboard storage and handling. Hydrogen can be stored as a high-pressure gas, as a liquid, or as a metal hydride. All three storage methods present problems either in safety, container weight, handling, or materials. An alternative approach would be to store the hydrogen in a chemical compound that could be safely handled and easily converted into hydrogen. Such a compound is methanol:

(1) Methanol is a renewable fuel that can be obtained from such natural products as wood, compost, or municipal trash.

(2) A mixture of methanol and water is readily converted to hydrogen by moderate temperatures and a catalyst.

(3) Methanol can be safely handled and easily stored by conventional methods.

(4) The amount of hydrogen stored per unit volume of liquid is 40 to 50 percent greater for methanol or methanol-water than for liquid hydrogen.

(5) If the energy necessary for the dissociation were waste thermal energy, the dissociation of methanol could serve as a vehicle for converting waste thermal energy into useful chemical energy. A 13 to 20 percent gain in energy is possible.

These advantages make methanol dissociation a viable approach for onboard hydrogen generation.

An experimental program (ref. 1) to study the performance of an internal combustion engine operating on a mixture of hydrogen and gasoline was started at the Lewis Research Center. The hydrogen used in this program was obtained by catalytic decomposition of methanol. At the same time, experiments were undertaken at this center to obtain data to design an efficient hydrogen reactor. A literature search showed that although steam reformation of methanol is well known and easily done, very little information is available on the details of the process. This report suggests a catalyst to use, shows how to monitor the reactor temperature, and suggests a way to obtain very high hydrogen space velocities at high methanol conversions from a given reactor design.

Data were taken in U.S. customary units and converted to SI units for this report.

EXPERIMENTAL APPARATUS AND PROCEDURE

The experimental setup used for this study is shown in figure 1. Feedstock was delivered to the system by a calibrated metering pump. The feed passed through a rotameter to a vaporizer and entered the reactor at the back of the furnace. The reactants and unreacted gases were then cooled by a cold-water condenser. The unreacted methanol and water were condensed and collected in a cold trap (liquid collector) maintained at about 263 K by an ice-brine mixture. The noncondensible gases (hydrogen (H_2), carbon monoxide (CO), and carbon dioxide (CO_2)) were then passed through a calibrated, wet test meter that measured the volume of gas produced. A tap was located between the liquid collector and the wet test meter so that the product gases could be diverted to a gas chromatograph for analysis.

The methanol was certified electronic grade and had a stated purity of 99.5 percent. An equimolar mixture of methanol and distilled water was prepared by combining calculated volumes of the two components. Because a volume reduction occurs when the two liquids are mixed, the density had to be determined by the weight fraction of

methanol in the mixture and tables in Lange's handbook (ref. 2).

The reactor (fig. 2), a 2.5-centimeter-inside-diameter copper tube, was nickel plated on the outside to protect it from high-temperature corrosion. The catalyst was contained in the tube by a permanent screen at the catalyst-bed inlet and a movable screen at the catalyst-bed outlet. The outlet screen could be adjusted to accommodate various catalyst lengths. Soft copper rings insured a good seal at the flange. The completely assembled reactor was always pressurized and bubble checked to insure a leak-tight system.

The temperature profile through the reactor was mapped by seven thermocouples. Five measured the centerline gas temperature; two others measured the reactor skin temperature. Thermocouple 1 measured the gas temperature 2.5 centimeters before the bed; thermocouple 5 measured the reactor outlet temperature. Thermocouples 2, 3, and 4 were located 2.5, 7.6, and 12.7 centimeters, respectively, after the start of the bed. Skin temperatures were measured 4.6 and 11.4 centimeters after the start of the bed. The outputs from these thermocouples were fed to a digital thermometer that had a 355 K furnace as a reference junction. A Lewis switch allowed switching from one thermocouple to another. A thermocouple mounted in the wall of the furnace was used to control the furnace temperature. So that the furnace temperature would be known as well as the reactor temperatures, an additional thermocouple was located at the same place as the furnace thermocouple and was monitored by the digital thermometer. The controller allowed the furnace temperature to vary about ±6 K.

A brief survey of available commercial catalysts indicated that copper chromite would yield good results. Two hundred grams of copper chromite catalyst, occupying a volume of 0.0924 liter, was used in these tests. The catalyst, manufactured by Harshaw Chemical Company, was in cylinders 0.32 centimeter high by 0.32 centimeter in diameter. It was designated Cu-0203 T (1/8) and contained about 78-percent CuO, 20-percent Cr_2O_3, and 2-percent graphite. The graphite served as a lubricant for the dies during catalyst manufacture. The catalyst was shipped in the oxidized state and had a bulk density of 2163 kilograms per cubic meter. According to Baker and Doerr (ref. 3), the fresh catalyst properties were

Hardness, kg	11
Surface area, m^2/g	4
Pore volume, cm^3/g	0.16
Mean pore radius, Å	780

The oxidized catalyst had to be reduced before it could be used. Considerable care had to be used in reducing the catalyst since the reduction process is exothermic and the heat liberated is sufficient to raise the reactor temperature to well over 800 K. At

these high temperatures, the copper in the catalyst would be sintered and result in a loss in activity. Hydrogen or carbon monoxide was suggested as the reducing agent, but metering and safety requirements made it desirable to seek another agent. Tests showed that a lean mixture of methanol and water (10-percent methanol by volume) would reduce the catalyst. The experimental procedure used for the reduction was as follows: Initially, the reactor was brought to about 505 K and a nitrogen flow of 3 liters per minute was established. Then 20 milliliters per hour of the methanol-water feed was added. The progress of the reduction through the reactor can be followed by observing the rise and fall of the temperature at each thermocouple. The reactor temperature was never allowed to exceed 589 K during the reduction. After the initial rapid reduction passed through the reactor (about $1\frac{1}{2}$ hr for 200 g of catalyst), a slow reduction took place that required about 4 more hours.

The gaseous products from the reactor were analyzed on a gas chromatograph that was modified for the task. Helium was used as the carrier gas, and a polarity switch was required to detect the hydrogen. A Porapak Q packing was used in the 3.96-meter-long column, which was maintained at room temperature. This length and temperature gave complete separation of all the species. The analysis required about 20 minutes. A standard mixture was prepared of all the gases in concentrations like those expected in the test runs. This standard mixture was always run through the chromatograph twice at the beginning of the day and once or twice at the end. So that a good sample would be obtained from the reactor, the product gases were flushed through the sample loop for about 15 minutes.

To simplify the data-taking procedure, the volumetric data and the gas analysis data were taken in separate experiments. The two sets of data were then related to each other by the measured feed space velocity. Figure 3 shows the normalized, measured mole fractions of each species as a function of feed space velocity. Because smooth curves can be drawn through the data, it was not necessary to duplicate every data point taken in the volumetric experiments. The concentrations reported in table I were taken from curves such as these.

To obtain accurate measurements of the volumetric conversion rate, it was important to know exactly how much gas was produced for a given amount of liquid metered to the system. Tests showed that the reproducibility of the metering pump was not good enough to make an accurate determination of the liquid delivered. Therefore, a variation of the bucket-and-stop-watch methods shown in figure 4, was devised. The method uses two glass tubes, a volumetric flask, a three-way Teflon stopcock, and a metering pump. Tube B serves as a reservoir for establishing steady-state conditions in the reactor. Tube A has a line etched around it which serves as a start-and-stop marker. The procedure used was to start with tube A filled to the marker and then, as liquid is consumed, to add the feed from the volumetric flask. Time zero was when

the stopcock was turned from tube B to tube A. The delivery time was measured when the liquid level returned to the mark. In effect, this arrangement calibrated the metering pump for each run. Generally, 100 milliliters of liquid were used for each run.

A typical data set for each run is given in table II. The data consist of the start and stop times for delivering 100 milliliters of feed, the time to produce 15 liters of product gases, and eight thermocouple readouts. Because the recorded data varied slightly during the run, average values of the readings were used in the data reduction. The volume of gas measured by the wet test meter was corrected for atmospheric pressure, temperature, and the saturated vapor pressure of water and was recorded as STP liters in table I.

EXPERIMENTAL RESULTS

Methanol decomposition. - Methanol decomposes through either a dehydrogenation or a dehydration mechanism. The dehydrogenation mechanism involves formaldehyde as an intermediate; the reactions are

$$CH_3OH \rightarrow CH_2O + H_2 \tag{1}$$

$$CH_2O \rightarrow CO + H_2 \tag{2}$$

Adding water to the reaction removes the carbon monoxide by the well-known water-gas shift reaction

$$CO + H_2O \rightleftarrows CO_2 + H_2 \tag{3}$$

The expected products from such a mechanism would be H_2, CO, CO_2, and CH_2O. The dehydration mechanism involves dimethyl ether as an intermediate; the reactions are

$$2CH_3OH \rightarrow CH_3OCH_3 + H_2O \tag{4}$$

$$CH_3OCH_3 \rightarrow CH_4 + CO + H_2 \tag{5}$$

and

$$CO + H_2O \rightleftarrows CO_2 + H_2 \tag{3}$$

In this case the expected products would be H_2, CO, CO_2, CH_4, and CH_3OCH_3.

A mass spectrometric analysis of the reaction products showed the major species to be hydrogen, carbon monoxide, and carbon dioxide. Only trace amounts of methane

were found and no formaldehyde or dimethyl ether. If formaldehyde or dimethyl ether were present, they would have been detected since unreacted methanol did appear in the analysis.

Since neither of the intermediates could be detected, the proposed mechanism was arrived at by considering the small fraction of methane found in the product gases. The dehydration mechanism (reactions (4), (5), and (3)) suggests that there should be a large amount of methane in the reaction products. Since only trace amounts of methane were found, the mechanism for the decomposition of methanol on a copper chromite catalyst must be dehydrogenation. Combining reactions (1) and (2) yields

$$CH_3OH \rightarrow CO + 2H_2 \qquad (1,2)$$

$$CO + H_2O \rightleftarrows CO_2 + H_2 \qquad (3)$$

The traces of methane measured probably resulted from the methanation reaction

$$CO + 3H_2 \rightleftarrows CH_4 + H_2O \qquad (6)$$

The amount of hydrogen produced was a function of two variables, the fraction of methanol converted α and the fraction of water consumed β. (Symbols are defined in appendix A.) Equations developed in appendix B can be used to calculate how α and β affect the experimentally measured parameters (1) product distribution, (2) volume of gaseous products, and (3) volume of unreacted feed. Table III shows how these variables changed as the values of α and β changed. Clearly, for the maximum hydrogen production, the best conditions are $\alpha = 1$ and $\beta = 1$. Here only hydrogen and carbon dioxide are present. For maximum energy enrichment ($\alpha = 1$ and $\beta = 0$), less hydrogen is produced and water and carbon monoxide are present. The last calculation is for $\alpha = 0.9$ and $\beta = 0.8$, a likely test condition. Here, even though less methanol is converted, more hydrogen is obtained than when $\alpha = 1$ and $\beta = 0$. In addition, table III is a guide for checking the consistency of the data: Once values of α and β are determined, all the other parameters must behave in a set pattern. An inconsistency in one parameter is strong reason to recheck the data. Failure to do this could lead to an incorrect conclusion.

An example of an inconsistency in data can be found in the work of Kester, et al. (ref. 4). They studied the same reaction on a copper - zinc oxide catalyst and reported methanol conversion α of 0.987. They reported a gas analysis of 0.76 hydrogen, 0.003 carbon monoxide, 0.23 carbon dioxide, and no CH_4, CH_2O, or ether. Thus, it can be assumed that the dehydrogenation mechanism probably applies to their data. Of the 823 cubic centimeters of feed that was used, they collected 200 cubic centimeters

of liquid, 96 percent of which was water. This is a large amount of water to have left since the original 823 cubic centimeters of feed contained only about 260 cubic centimeters of water. The mechanism shows that large carbon monoxide concentrations would be expected for small water consumption. If a value for β is calculated from these data ($\beta = 0.28$, eq. (B5)), the product gas composition can be calculated. For $\alpha = 0.987$ and $\beta = 0.28$, the product gas composition should be 0.70 hydrogen, 0.22 carbon monoxide, and 0.09 carbon dioxide. Because the experimental value of 0.003 for carbon monoxide is significantly different from the calculated value of 0.22, there is a strong possibility of a discrepancy in the reference 4 data.

Calculation of α and β from experimental data. - As discussed previously, α and β can be determined by the composition of the product gases and the volume of either the gas or the condensate. In this study the volume of the gas produced by 100 milliliters of feed was used. This measurement can be made extremely accurate (less than 1 percent error). The time to deliver the 100 milliliters was known to within a few seconds, and the volume of gas was known to less than 0.1 liter. The volume of condensate was not measured because not all the condensate could be collected. Figure 5 shows that at 263 K the vapor pressure of methanol is significant, and about 4 percent (27.5/760) of the gas passing through the trap would be methanol. With 150 liters of gas being produced by the 100 milliliters of feed, about 8 milliliters of methanol could be lost from the condensate. This amount could significantly affect the measured conversion.

The fraction of methanol converted α in the reaction can readily be calculated from the postulated mechanism. Reaction (1, 2) shows that every mole of methanol that dissociates yields 3 moles of gas (one carbon monoxide and two hydrogen). Since the carbon monoxide that reacts by reaction (3) replaces itself with hydrogen, the sum of the moles of these two gases is unaffected by reaction (3). Thus

$$\alpha = \frac{N_{H_2} + N_{CO}}{3N_{CH_3OH}} \tag{7}$$

where N_{CH_3OH} is the number of moles of methanol delivered to the reactor.

The number of moles of each species N_i can be replaced by its corresponding space velocity Sv(i).

$$\alpha = \frac{Sv(H_2) + Sv(CO)}{3Sv(CH_3OH)}$$

where the space velocity is defined as the volume of reactant or product measured at

standard conditions, per unit time per unit volume of reactor.

$$Sv(H_2) = \frac{\text{Volume of } H_2 \text{ (STP liters)/hr}}{\text{Bulk volume of catalyst (liters)}} \tag{9}$$

$Sv(CO)$ and $Sv(CO_2)$ are calculated in the same way.

$$Sv(CH_3OH) = \frac{(\text{Moles of } CH_3OH) \times 22.4/\text{hr}}{\text{Bulk volume of catalyst (liters)}} \tag{10}$$

The standard conditions for measuring the volumes of reactants and products were a temperature of 273.2 K, a pressure of 1 atmosphere, and the gaseous state.

The fraction of water consumed β was calculated from the measured quantity of gas produced by 100 milliliters of feed, as follows: One-hundred milliliters of feed contains x moles of methanol, and the volume of gas produced by this 100 milliliters is V_{100}:

$$V_{100} = x(3\alpha + \beta)(22.4) \tag{11}$$

The maximum volume of gas that can be produced from this 100 milliliters of feed is $\alpha = 1$ and $\beta = 1$:

$$V_{max} = x(4)(22.4) \tag{12}$$

The ratio of these two volumes yields a relationship for $3\alpha + \beta$:

$$4\,\frac{V_{100}}{V_{max}} = 3\alpha + \beta \tag{13}$$

where V_{100} is measured, and V_{max} is calculated from the feed composition and density. Values of $3\alpha + \beta$ are given in table IV, along with the experimentally determined values of α and β. These experimental values were then checked by calculating the mole fractions of carbon dioxide in the product gases and comparing them with the experimental ones. As shown in table III and appendix B, the mole fraction of this gas is related to α and β by

$$\chi_{CO_2} = \frac{\beta}{2\alpha + \beta} \tag{14}$$

Table IV shows excellent agreement between the mole fractions of carbon dioxide

measured by the gas chromatograph and those calculated by using equation (14) and α and β. This comparison serves as a reliable check on the values of α and β since the mole fraction of carbon dioxide does not appear in the equations used to determine α and β.

Temperature. - It is important to know the reaction temperature since most reaction rates are an exponential function of the temperature. However, in the case where a high methanol conversion is desired and a large reactor is used, the temperature is difficult to define because it is not constant over the length of the reactor. Figure 6 is a typical temperature profile observed for methanol dissociation. Since the dissociation of methanol vapor is endothermic by 93.7 kilojoules per mole (22.4 kcal/mole), energy must be supplied to the reactants. This energy is supplied by the furnace by means of heat conduction through the catalyst. As a result the temperature is expected to be low at the reactor inlet. As the concentration of methanol decreases through the reactor, the amount of energy extracted by the reaction decreases and the temperature rises.

The measured temperatures in the reactor for each run are given in table V. The runs at various feed space velocities for the three furnace temperatures are shown in figure 7. For illustrative purposes, the profile near the reactor inlet was estimated so that the magnitude of the temperature drop could be visualized (fig. 7(c)). In constructing the profile, it was assumed that the lowest temperature would occur about 0.64 centimeter after the start of the catalyst bed and that the lowest temperature would be the same for all runs at a given furnace temperature. The average reactor temperature was taken to be the average of the three measured bed temperatures (T_2, T_3, and T_4). These values are also given in table V. The data in table V show that the average reactor temperature is a function of the feed flow rate and the furnace temperature.

Two skin temperature measurements (4.6 and 11.4 cm after the start of the bed) were taken for each run. The curves in figure 7 were used to determine the centerline, or gas, temperature at each of these positions. These temperatures, along with the temperature difference ($T_S - T_g = \Delta T$), are shown in table V. It is interesting that the ΔT at the 4.6-centimeter position reaches a constant value at the higher feed flow rates even though the skin temperature continues to decrease. A plot of ΔT versus feed space velocity for the three furnace temperatures is shown in figure 8. The point at which ΔT reaches a maximum corresponds to a methanol conversion of 0.92 to 0.95 for each furnace temperature. The maximum value of ΔT increased as the furnace temperature increased.

Volume of gas. - The volumes of gas (in STP liters) evolving from 100 milliliters of solution for each furnace temperature are tabulated in table I and plotted in figure 9 as a function of feed space velocity. Smooth curves could be drawn through all the data

points. Each curve goes through a maximum value that corresponds to the space velocity necessary to completely utilize all the 200 grams of catalyst. It is interesting that both slower and faster flow rates yield less gaseous products. At faster flow rates, the falloff is due to a drop in the fraction of methanol converted because of the combined effect of a shorter dwell time and a lower average reactor temperature. Complete conversion occurs at the slower flow rates, but undesirable side reactions adversely affect the product distribution because of the higher average reactor temperatures. Since the equilibrium for reaction (3) has a negative temperature dependence, the higher reactor temperatures will force the reaction to the left and will thus result in less noncondensible products. Higher temperatures favor methane formation, probably by way of reaction (6), which also results in less noncondensible products. This type of data has been useful in promoting an understanding of the chemistry involved in methanol dissociation.

DISCUSSION

The primary purpose for studying the steam reformation of methanol was to obtain data for the design of a reactor for onboard hydrogen generation. Such a reactor, designed to produce a given amount of hydrogen, should be as small as possible and use a minimum amount of feed. The data from this study can be used to establish the operating conditions necessary to accomplish this.

Figure 10 shows the hydrogen space velocity as a function of feed space velocity for the three furnace temperatures. As can be seen, the hydrogen output increases as the feed space velocity increases. Extending the data to higher feed space velocities would increase the hydrogen output per unit of time but would be wasteful since the fraction of methanol converted decreases. However, the data show that increasing the furnace temperature will significantly increase the hydrogen output at higher feed space velocities. This suggests that still higher temperatures should be used, although possible disadvantages to using higher temperatures are

(1) Sintering of the catalyst - The active part of the copper chromite catalyst is thought to be the reduced copper. It is known that metal catalysts are prone to sintering at high temperatures. Such sintering would remove active sites and tend to reduce catalyst surface area and thus catalyst activity.

(2) The formation of undesirable products - At high temperatures, methane will be formed by the reaction

$$CO_2 + 4H_2 = CH_4 + 2H_2O$$

which removes 4 moles of hydrogen for every mole of methane formed. This would

reduce the apparent catalyst performance.

(3) The water-gas shift reaction - The equilibrium for reaction (3) shifts to the left as the temperature increases and lowers the hydrogen yield.

The experimental data for each furnace temperature show that the average reactor temperature decreased as the feed space velocity increased. This is to be expected since the dissociation of methanol is endothermic and removes heat from the reactor. The dependence of the reactor temperature on the feed space velocity suggests that higher furnace temperatures can be used if the feed space velocity is properly adjusted. The temperature maintained in the reactor would be one that maximized the hydrogen output but minimized the drawbacks of higher temperatures.

Selection of probe to monitor temperature. - Since the reactor temperature is so important, a probe must be selected to monitor it. Probe 4 (fig. 2) was chosen to do this. Probe 2 was not chosen because it was too close to the reactor inlet and very insensitive to the changing flow rates. Probe 3 could have been chosen since it measures a temperature quite close to the average reactor temperature, but it is probably also too close to the reactor inlet. Probe 5 was removed as a candidate because it was difficult to ascertain whether it was reading the gas temperature alone. The reason is that probe 5 had to be placed on the metal used to mount the catalyst retainer screen and might have been influenced by the temperature of the mount. Probe 4 is located 12.7 centimeters after the reactor inlet and 5.08 centimeters before the outlet.

Although the position of the monitoring probe was selected by a process of elimination, the choice turned out to be an extremely good one. This can be seen by the three correlations of the data obtained with this probe temperature:

(1) The mole fraction of carbon monoxide in the product gases (fig. 11) yielded a smooth curve when plotted as a function of the temperature measured by probe 4. This was not true for any of the other probe temperatures.

(2) The energy absorbed by the reaction is closely related to the difference between the probe temperature T_4 and the furnace temperature T_F. The temperature and gas composition at the reactor inlet and outlet are known, and thus the enthalpy at each of these positions can be calculated. The difference in these enthalpies is the amount of energy absorbed by the reaction Q. The following table shows these values for three experiments at the same T_4. When Q and $T_F - T_4$ are normalized by the first run, the ratios (columns 7 and 9) are very similar. This relation occurs only when comparing data at the same value of T_4.

Furnace temperature, T_F, K	Run	Temperature at probe 4, T_4, K	Methanol space velocity, Sv (CH_3OH), hr^{-1}	Fraction of methanol converted, α	Amount of energy absorbed by reaction, Q, kJ	Amount of energy absorbed by reaction normalized to value at reactor inlet, Q_i/Q_1	Difference between T_F and T_4, K	Normalized temperature difference, $\frac{(T_F - T_4)_i}{(T_F - T_4)_1}$
630	4	552	1320	0.952	165.7	1.0	78.4	1.0
653	5	552	1807	.919	215.4	1.30	100.6	1.28
680	16	551	2549	.879	277.0	1.67	129.4	1.65

(3) In a later section the hydrogen and methanol space velocities are empirically found to fit the equation

$$Sv = A \exp\left(-\frac{\omega}{T_4}\right)$$

where α is a constant. If the constant ω were assumed to be the activation energy for the methanol dissociation, an average value of 64.4 kilojoules per mole (15.4 kcal/mole) would be obtained. This value compares quite well with the 59.0 kilojoules per mole (14.1 kcal/mole) reported by Bond (ref. 5).

Selection of optimum reactor operating temperature. - The temperature 589 K was selected as the optimum reactor operating temperature. This temperature appeared to be high enough for good reactor operation and yet low enough to prevent significant sintering of the catalyst and to minimize other problems associated with high temperatures. After the catalyst was tested in an on-and-off mode for more than 100 hours, some loss in activity was observed (about 5 to 10 percent). This loss probably happened during the low-feed-flow-rate experiments, where measurements showed that the latter part of the bed experienced temperatures near 644 K. During these tests, about 75 percent of the catalyst was above 589 K. Now, the loss in activity seemed too small to be associated with the 589 K zone but might be reasonable for the 644 K zone. For this reason, we concluded that the catalyst would not sinter as long as the temperature did not exceed 589 K.

The analysis of the gaseous products showed a methane concentration of 0.02 percent or less at 589 K. This concentration is small and should have negligible effect on the hydrogen production. Figure 11 shows about 4-percent carbon monoxide in the

product gases at 589 K. From approximate calculations, this much carbon monoxide in the exhaust gases decreases the hydrogen space velocity by about 5 percent. Even though this seems like a large loss, it must be remembered that carbon monoxide cannot be completely eliminated as a product. Even at 552 K, about 1 percent was measured. Since the hydrogen output can be increased about 300 percent by increasing the reactor temperature from 552 K to 589 K (fig. 15(a)), the 5-percent loss is a small price to pay.

CORRELATION AND EXTRAPOLATION OF EXPERIMENTAL DATA

The hydrogen space velocity at the working temperature of 589 K (probe 4) could not be measured because of apparatus limitations. Thus it had to be calculated from empirical equations determined for the low-temperature data. The usual procedure for such a calculation is to obtain a kinetic rate equation from the experimental data and extrapolate it to the higher temperature.

Darby and Kemball (ref. 6) studied the decomposition of methanol on a cobalt Fischer-Tropsch catalyst and found the overall kinetics were described by the equation

$$\frac{-d[CH_3OH]}{dt} = \frac{k[CH_3OH]}{1 + b[CO]} \tag{15}$$

The water in the present experiment removes the inhibiting effect of the carbon monoxide and makes the dissociation a simple first-order reaction:

$$CH_3OH + H_2O \rightarrow CO_2 + 3H_2 \tag{16}$$

Levenspiel (ref. 7, p. 111) presents an equation for the rate constant of a first-order irreversible reaction that for the present study becomes

$$k = Sv(CH_3OH)\left(2 \ln \frac{1}{1 - \alpha} - \alpha\right) \tag{17}$$

Rate constants k calculated from the experimental data by using equation (17) were fitted to the Arrhenius equation

$$k = A \exp\left(-\frac{\Delta E}{RT}\right) \tag{18}$$

by plotting ln k versus $1/T_4$. A least-squares fit to the data yielded an activation energy of 37.7 kilojoules per mole (9 kcal/mole), which is not close to the 59.0 kilo-

joules per mole (14.1 kcal/mole) reported by Bond (ref. 5).

Kinetic data in tube reactors are usually obtained by using small bed sizes and high feed flow rates. At those conditions, the conversion is low, but the reactor temperature is uniform and can be measured. The present study is different. A large catalyst bed was used, and the feed space velocities were such that methanol conversions were high. These conditions resulted in a large temperature gradient in the catalyst bed (fig. 6). Under these conditions it is clear why equations (17) and (18) failed to yield an activation energy that agreed with published results.

Empirically it was found that the hydrogen and methanol space velocities could be correlated with the temperature T_4 if only data at the same value of α were compared. Three furnace temperatures were used in these experiments, and the temperature T_4 was observed to be a function of the fraction of methanol converted α, the feed space velocity, and the furnace temperature (fig. 12). Thus for a given value of α, there are three space velocities and three temperatures T_4, one for each furnace temperature. Accurate values of T_4, $Sv(H_2)$, and $Sv(CH_3OH)$ were obtained from plots (fig. 13) of each parameter versus α. The data and the least squares fit to the equation

$$Sv(i) = A \exp\left(\frac{-\omega}{T_4}\right) \tag{19}$$

where i is hydrogen or methanol, are shown in table VI. The hydrogen space velocity behaved in the same manner as the methanol space velocity. This is to be expected since the postulated mechanism (appendix B) shows that the hydrogen space velocity is $2\alpha + \beta$ times the methanol space velocity, and data points at the same α have the same value for β. For example,

Furnace temperature, T_F, K	Run	Fraction of methanol converted, α	Fraction of water consumed, β	$2\alpha + \beta$	Temperature at probe 4. T_4
630	5	0.922	0.881	2.725	544
680	8	.923	.883	2.729	563

That these space velocities can be plotted in the same manner as a rate constant is not unexpected since equation (17) shows that, for a constant α, these space velocities are proportional to the rate constant.

Figure 14 shows $\ln Sv(H_2)$ versus $1/T_4$ for various values of α. These data fall precisely on the least-squares line. It is this fit that leads us to believe that good extrapolations can be obtained with the equations even though only three data points were used for each line. The values of ω and A change as α changes, and the hydrogen and methanol space velocities must be calculated for each value of α. It may be noted that if ω is assumed to be $\Delta E/R$, an average value of 64.6 kilojoules per mole (15.4 kcal/mole) is obtained for the activation energy. This is close to the value of 59.0 kilojoules per mole (14.1 kcal/mole) reported in the literature.

Extrapolated values of the hydrogen and methanol space velocities at the optimum reactor operating temperature of 589 K are plotted versus α in figure 15. Each calculated curve was joined to an experimental data point at this temperature by a dashed line. Although it would be desirable to confirm these curves with experimental data, these velocities were well beyond the limitations of the experimental apparatus. However, it is possible to check the consistency of the two curves. Previously it was shown that the hydrogen space velocity was proportional to the methanol space velocity

$$(2\alpha + \beta)Sv(CH_3OH) = Sv(H_2) \tag{20}$$

The proportionality constant $2\alpha + \beta$ can be calculated for each value of α on the curve from the measured mole fraction of carbon monoxide in the exhaust gases at 589 K (fig. 11) and from the definition $\chi_{CO} = (\alpha - \beta)/(3\alpha + \beta)$ (table III). With values of $2\alpha + \beta$ calculated in this manner, $Sv(H_2)$ can be calculated from equation (2) by using values of $Sv(CH_3OH)$ from figure 15(b). Similarly, $Sv(CH_3OH)$ can be calculated from equation (2) by using values of $Sv(H_2)$ from figure 15(a). Values of $Sv(H_2)$ and $Sv(CH_3OH)$ calculated in this manner are plotted as circles in figure 15 for comparison with the curves obtained from the extrapolation procedure. The largest discrepancy, which appears at a methanol conversion α of 0.87, indicates an uncertainty of about 4 percent for $Sv(H_2)$ (fig. 15(a)). For $\alpha > 0.88$, the agreement is excellent. Figure 19 also contains a curve calculated for 552 K for which experimental data were available for comparison. The data fit the curve very well.

Energy enrichment calculation. - The dissociation of methanol is an endothermic reaction, that is, energy must be added to the system for a reaction to occur. This added energy increases the heat content of the products and thus their combustion energy. If waste energy were used as the energy necessary for the dissociation, the dissociation of methanol could be a means of converting waste thermal energy into useful chemical energy. Such a situation occurs with internal combustion engines, where

the hot exhaust gases are considered waste and vented to the atmosphere. Sufficient thermal energy is available in these gases to reform enough methanol so that the engine could be run entirely with hydrogen. The advantages of this mode of operation were pointed out by Kester, et al. (ref. 4).

The energy enrichment E_R is the ratio of the heat of combustion of the reformer products to the heat of combustion of the tank liquid. The energy gained depends on the fate of the methanol in the reactor:

(1) Methanol is unconverted:

$$CH_3OH \rightarrow CH_3OH$$

(2) Methanol reacts to form the products of reaction (1, 2):

$$CH_3OH \rightarrow CO + 2H_2 \qquad (1,2)$$

(3) Methanol reacts to form the products of reaction (1, 2) followed by the carbon monoxide reaction (3):

$$CH_3OH + H_2O \rightarrow CO_2 + 3H_2 \qquad (1,2) + (3)$$

The heats of combustion of the product gases for these three cases at 300 K are

(1) 638.5 Kilojoules per mole of CH_3OH (152.6 kcal/mole of CH_3OH) for the reaction

$$CH_3OH(\text{liquid}) + \frac{3}{2}O_2 \rightarrow CO_2 + 2H_2O$$

(2) 766.5 Kilojoules per mole of CH_3OH (183.2 kcal/mole of CH_3OH) for the reaction

$$CO + 2H_2 + \frac{3}{2}O_2 \rightarrow CO_2 + 2H_2O$$

(3) 725.1 Kilojoules per mole of CH_3OH (173.3 kcal/mole of CH_3OH) for the reaction

$$CO_2 + 3H_2 + \frac{3}{2}O_2 \rightarrow CO_2 + 3H_2O$$

The energy enrichment for each path is

(1) $E_R = -152.6/-152.6 = 1.000$

(2) $E_R = -183.2/-152.6 = 1.201$

(3) $E_R = -173.3/-152.6 = 1.136$

The fraction of methanol apportioned to each path is determined by the values of α and β. The fraction of methanol unconverted is $1 - \alpha$, the amount that goes by path 2 is $\alpha - \beta$, and the amount that goes by path 3 is β. Thus the energy enrichment for a given case is

$$E_R = (1 - \alpha)1.00 + (\alpha - \beta)1.201 + (\beta)1.136 \qquad (21)$$

For example, run 8 at $T_F = 630$ K ($\alpha = 0.804$, $\beta = 0.783$) yields $E_R = 1.11$, an 11-percent increase.

The energy enrichment for each experimental run was calculated (table IV). It is important to point out that the original methanol feed was liquid and that some of this energy enrichment includes the heat of vaporization of the methanol.

Sizing a reactor. - As an example, the results of this report were used to size a reactor for the requirements in reference 1: an onboard reactor that is as small as possible yet capable of producing 7630 STP liters (1.5 lb) of hydrogen per hour. This hydrogen will be added to gasoline, and the engine will be operated very lean.

At 589 K and $\alpha = 0.87$, a hydrogen space velocity of 9400 per hour can be obtained (fig. 15(a)). The volume of catalyst needed to produce this much hydrogen is calculated from

$$Sv(H_2) = 9400\ hr^{-1} = \frac{(\text{STP liters of } H_2)/hr}{\text{Liters of catalyst (bulk volume)}}$$

and is 7630/9400 = 0.81 liter. The methanol space velocity is 3800 per hour (fig. 15(b)) and the feed flow rate is calculated from

$$Sv(CH_3OH) = 3800\ hr^{-1}\ \frac{(\text{Moles of } CH_3OH) \times (22.4)/hr}{\text{Bulk volume of catalyst}}$$

and is 3800 (0.81/22.4) = 137.4 moles per hour. Now, since 1 liter of feed equals 17.7 moles of methanol, the volume of feed is 137.4/17.7 = 7.76 liters per hour (2.05 gal/hr).

The amount of catalyst needed (0.81 liter) can be put into nine 17.8-centimeter-long tubes 2.54 centimeters in inside diameter. A probe should be installed in the catalyst bed 5.08 centimeters from the end. This probe would be used to regulate the heat flow to the reactor to maintain a reactor operating temperature of 589 K. The heat of combustion of the reactor products (converted and unconverted) is 12 to 13 percent higher than the heat of combustion of the incoming feed.

CONCLUSIONS

The steam reformation of an equimolar mixture of methanol and water on a copper chromite catalyst was studied at three furnace temperatures and feed space velocities from 800 to 2600 per hour. Empirically, it was found that the hydrogen space velocity could be related to the temperature recorded by a probe 12.7 centimeters after the reactor inlet and 5.08 centimeters before its outlet by the equation

$$Sv(H_2) = A \exp\left(\frac{-\omega}{T_4}\right)$$

where A and ω are functions of the fraction of methanol converted α, and T_4 is the temperature at probe 4. A hydrogen space velocity of 9400 per hour could be attained with a reactor temperature of 589 K and an α of 0.87. Because only one reactor configuration was used, it is not clear how these results will hold for other configurations.

A pseudoequilibrium constant that corresponded to temperatures 83 K lower than those measured in the gas was calculated for the water-gas shift reaction (appendix C). It is known that a temperature gradient in a catalyst pellet results when an endothermic reaction occurs in the pores of the catalyst. A temperature difference between the gas and the pore wall of 68 K was calculated for methanol dissociation in this experiment. It is not known how much methanol reacts in the pores, but it was clear that the water-gas shift reaction occurs primarily in the pores.

The size of an onboard hydrogen generator to produce 7630 STP liters (1.5 lb) of hydrogen per hour was estimated. The amount of catalyst needed could be confined in nine tubes 17.8 centimeters long and 2.5 centimeters in inside diameter.

Eighty-seven percent of the methanol would be converted to hydrogen and other gaseous products. The products coming out of the reactor would contain 12 to 13 percent more chemical energy than the incoming methanol and water. The reactor temperature should be controlled by a probe mounted 5.08 centimeters before the reactor outlet.

Lewis Research Center,
National Aeronautics and Space Administration,
Cleveland, Ohio, March 10, 1978,
776-71.

APPENDIX A

SYMBOLS

A	concentration at surface of catalyst pellet
b	constant
C_c	concentration at center of pore
C_s	concentration at surface of catalyst pellet
D	Knudsen diffusion coefficient
E_R	energy enrichment, E_{out}/E_{in}
ΔE	energy of reaction, J/mole (cal/mole)
ΔH	energy of reaction, J/mole (cal/mole)
k	rate constant
N_i	number of moles, where $i = H_2$ or CH_3OH
N_{NC}	number of moles of noncondensible gases
N_T	total number of moles of product and reactant
Q	amount of energy absorbed by reaction
R	gas constant
$Sv(CH_3OH)$	methanol space velocity
$Sv(H_2)$	hydrogen space velocity
T	temperature, K
T_c	temperature at center of pore, K
T_F	furnace temperature, K
T_g	temperature of gas
T_S	skin temperature, K
T_s	temperature at surface of catalyst pellet, K
T_{1-5}	temperature at probes 1 to 5, K
ΔT	change in temperature, kelvin
V	volume
V_{max}	maximum volume of gas from 100 milliliters of solution

V_{100}	measured volume of gas from 100 milliliters of solution
α	fraction of methanol converted
β	fraction of water consumed
λ	coefficient of heat conduction
χ	mole fraction
ω	exponential term in Arrhenius equation

APPENDIX B

EQUATIONS FOR CALCULATING EFFECT OF α AND β ON EXPERIMENTALLY MEASURABLE PARAMETERS

Mole fraction of each species. - The number of moles of each species per mole of methanol can be calculated by using the variables α and β, where α equals the fraction of methanol that reacts via reaction (1, 2) and β is the fraction of water consumed in reaction (3). For an equimolar mixture of methanol and water,

$$(1 - \alpha) \quad (\alpha) \quad (2\alpha)$$

$$CH_3OH \rightarrow CO + 2H_2$$

$$(\alpha - \beta) \quad (1 - \beta) \quad (\beta) \quad (\beta)$$

$$CO + H_2O = CO_2 + H_2$$

The number of moles of each species per mole of methanol at any time is

$$CH_3OH = 1 - \alpha$$

$$H_2O = 1 - \beta$$

$$H_2 = 2\alpha + \beta$$

$$CO_2 = \beta$$

$$CO = \alpha - \beta$$

The number of moles of noncondensible gases per mole of methanol (dry sample) is

$$N_{NC} = 3\alpha + \beta \tag{B1}$$

and the total number of moles of product and reactant (wet sample) is

$$N_T = 2 + 2\alpha \tag{B2}$$

The mole fraction of each gas can be expressed as either a dry or a wet mole fraction. For example,

$$\chi_{H_2}(\text{dry}) = \frac{2\alpha + \beta}{3\alpha + \beta}$$

$$\chi_{H_2}(\text{wet}) = \frac{2\alpha + \beta}{2 + 2\alpha}$$

Volume of noncondensible gases. - The volume (in STP liters) of noncondensible gases is calculated by

$$\frac{\text{Volume of noncondensible gases}}{\text{Moles of } CH_3OH} = (3\alpha + \beta) \times (22.4) \tag{B3}$$

Volume of unreacted liquid. - The calculation of the volume of unreacted liquid is more complicated because of volume contraction in the methanol-water system. The first step is to calculate the weight of each species left from a fixed volume of feed (in this case, 100 milliliters). For example,

$$\text{Grams of } CH_3OH = \frac{\text{Moles of } CH_3OH}{\text{100 Milliliters of feed}} \times (1 - \alpha)(\text{Molecular weight of } CH_3O_4) \tag{B4}$$

$$\text{Grams of } H_2O = \frac{\text{Moles of } H_2O}{\text{100 Milliliters of feed}} \times (1 - \beta) \times (\text{Molecular weight of } H_2O) \tag{B5}$$

The next step is to calculate the weight percent of methanol in the unreacted liquid. This value and tables in reference 2 will give the density of the solution. Finally, the volume of unreacted solution is its weight divided by its density. This calculation was made for each test run, and the results are shown in table IV.

APPENDIX C

PSEUDOEQUILIBRIUM CONSTANT AND TEMPERATURE GRADIENTS IN CATALYST PELLETS

A pseudoequilibrium constant for the water-gas shift reaction can be calculated from the experimental data. This pseudoequilibrium constant presents an interesting insight into the mechanics of the process and clearly shows that the shift reaction occurs in the pores of the catalyst. The equilibrium constant was calculated from the experimental data via the following equation:

$$K_{eq} = \frac{(CO_2)(H_2)}{(CO)(H_2O)} = \frac{\chi_{CO_2}\chi_{H_2}}{\chi_{CO}\chi_{H_2O}} \tag{C1}$$

where χ_i is the mole fraction of each gas. Because the experimental mole fractions were measured in a dry sample, they had to be converted to mole fractions in a wet sample. This was done by multiplying the dry mole fraction by the quantity $(3\alpha + \beta)/(2 + 2\alpha)$ (eqs. (B1) and (B2)). The mole fraction of water can be taken to be $(1 - \beta)/(2 + 2\alpha)$ (table III). Substituting these into equation (C1) gives

$$K_{eq} = \frac{\chi_{CO_2}\chi_{H_2}(3\alpha + \beta)}{\chi_{CO}(1 - \beta)} \tag{C2}$$

All these quantities were measured, except β, which was calculated from the data.

The data in tables I and IV were used to calculate the pseudoequilibrium constants that are tabulated in table IV. In figure 21 these equilibrium constants were plotted versus T_4 (the highest bed temperature and T_2 (the lowest bed temperature). The solid line is the theoretical curve for the equilibrium constant as a function of temperature. There is an apparent discrepancy because even the lowest bed temperatures are too high for the data to fit the curve. A plausible explanation for this behavior is discussed by Wheeler (ref. 8). He points out that when an endothermic reaction (the dissociation of methanol) occurs in the pores of a catalyst, the reaction temperature is much lower than the measured gas temperature in the bed. The reason is that nonmetallic catalysts are poor thermal conductors and the heat extracted by the reaction cannot be readily replaced. Thus, a temperature difference will exist between the walls of the pores and the gas outside the pores. The following equation was presented for calculating this temperature difference:

$$T_c - T_s = \frac{D\,\Delta H}{\lambda}(C_s - C_c) \qquad \text{(C3)}$$

where T_c and C_c are temperature and concentration at the center of the pore, T_s and C_s are at the surface of the catalyst pellet, and D is the Knudsen diffusion coefficient, ΔH is the energy of reaction in J/mole (cal/mole), and λ is the coefficient of heat conduction. Assuming C_c to be zero, we calculated a temperature difference of about 68 K for methanol dissociation on the pore walls. Now, if the shift reaction then occurs on these cool walls and goes to completion, its equilibrium temperature should correspond to that of the walls. The difference between the gas temperature T_4 and the temperature calculated from the pseudoequilibrium constant was about 83 K. This is in fair agreement with the theory, and we can conclude that the shift reaction is fast enough to go to completion and that it occurs in the pores of the catalyst, where the temperature is significantly lower than the gas temperature.

REFERENCES

1. Cassidy, John F.: Emissions and Total Energy Consumption of a Multicylinder Piston Engine Running on Gasoline and a Hydrogen-Gasoline Mixture. NASA TN D-8487, 1977.

2. Lange, Norbert Adolph, ed.: Handbook of Chemistry. Eighth Ed. Handbook Publishers, Inc., 1952.

3. Baker, Robert A.; and Doerr, Robert C.: Catalyzed Nitric Oxide Reduction with Carbon Monoxide. Ind. Eng. Chem. Process Des. Dev., vol. 4, no. 2, Apr. 1965, pp. 188-191.

4. Kester, F. L.; Konopka, A. J.; and Camara, E.: Automotive Storage of Hydrogen as a Mixture of Methanol and Water. TEC-75/004, Institute of Gas Technology, 1975.

5. Bond, G. C.: Catalysis by Metals. Academic Press Inc., 1962, p. 411.

6. Darby, P. W.; and Kemball, C.: Investigations of Reactions Along the Catalyst Bed in Flow Systems by Vapour-Phase Chromatography. Part 1, The Decomposition of Methanol on a Cobalt Fischer-Tropsch Catalyst. Trans. Faraday Soc., vol. 53, 1957, pp. 832-840.

7. Levenspiel, Octave: Chemical Reaction Engineering. John Wiley & Sons, Inc., 1962.

8. Wheeler, Ahlborn: Reaction Rates and Selectivity in Catalyst Pores. Catalysis, Vol. II, Fundamental Principles, part 2, Paul Hugh Emmett, ed., Reinhold Publishing Corp., 1955, pp. 105-165.

TABLE I. - EXPERIMENTAL FEEDSTOCK AND PRODUCT DATA

Run	Feed flow rate, milliliter/hr	Dry gas products					Feedstock		Products		
		Per 100 milliliters of feed	Per hour	H_2	CO	CO_2	Total	CH_3OH	H_2	CO	CO_2
		Volume, STP liters		Composition, percent by volume			Space velocity, hr^{-1}				
Furnace temperature, T_F, 630 K (675° F)											
1	96.7	151.9	146.1	74.4	4.3	21.4	827	414	1176	68.0	338
2	116.2	153.0	177.8	74.5	3.3	22.6	994	497	1434	63.5	435
3	135.7	151.6	205.8	74.5	2.3	23.4	1161	581	1659	51.2	521
4	154.3	148.0	228.4	74.6	1.7	23.8	1320	660	1844	42.0	588
5	172.5	144.1	248.6	74.7	1.1	24.1	1475	738	2010	29.6	648
6	189.7	139.2	264.1	74.7	.9	24.3	1623	812	2135	25.7	695
7	208.1	134.1	279.1	74.8	.7	24.5	1780	890	2260	21.1	740
8	235.1	126.3	297.0	74.9	.6	24.6	2012	1006	2408	19.3	791
Furnace temperature, T_F, 653 K (715° F)											
1	135.5	151.9	205.8	74.3	4.1	22.0	1162	581	1655	91.3	490
2	152.7	152.4	232.8	74.3	3.4	22.6	1310	655	1872	85.7	569
3	171.7	150.2	257.9	74.4	2.7	23.2	1473	736	2077	75.4	648
4	189.6	147.2	279.1	74.4	2.2	23.6	1626	813	2248	66.5	713
5	210.6	143.4	302.1	74.5	1.7	23.9	1807	903	2436	55.6	781
6	236.2	138.2	326.5	74.6	1.2	24.3	2026	1013	2636	42.4	859
7	258.4	134.0	346.3	74.6	1.0	24.5	2216	1108	2795	37.5	918
Furnace temperature, T_F, 680 K (765° F)											
1	134.5	147.2	198.0	72.9	7.1	20.3	1154	577	1562	152.1	435
2	152.3	149.8	228.2	73.0	6.2	21.0	1306	653	1803	153.1	519
3	170.8	150.6	257.2	73.1	5.4	21.7	1465	732	2035	150.3	604
4	180.0	150.3	270.5	73.1	4.9	22.0	1544	772	2140	143.4	644
5	187.9	150.2	282.2	73.2	4.5	22.3	1611	806	2236	137.4	681
6	208.6	149.7	312.3	73.3	3.7	22.9	1789	894	2477	125.1	774
7	231.2	148.0	342.2	73.4	2.9	23.6	1983	992	2719	107.4	874
8	255.9	144.7	370.3	73.5	2.3	24.0	2194	1097	2946	92.2	962
9	278.6	141.3	393.7	73.7	1.9	24.4	2390	1195	3141	81.0	1040
10	297.3	138.3	411.2	73.8	1.7	24.6	2549	1275	3285	75.6	1095

TABLE II. - EXPERIMENTAL DATA FOR ONE TEST RUN

[Room temperature, 74° F; ambient pressure, 29.2 in. of Hg; time to deliver 100 milliliters of feed, 9467 - 7380 = 2087 sec; feed flow rate, 100 × (3600/2087) = 172.5 milliliters/hr; volume of gas (expanded) = 10 × 15 + 15 (124/196.3) = 159.5 liters/100 milliliters of feed.]

Timer reading, sec	Time to produce 15 liters of product gases, sec	Thermocouple location							
		Inlet	Outlet	Center of catalyst bed			Skin		Furnace
				Distance from start of bed, in.					
				2	3	5	1.8	4.5	
		Thermocouple designation							
		T_1	T_5	T_2	T_3	T_4	T_6	T_7	T_F
		Temperature, °F							
[a]7380	---	---	---	---	---	---	---	---	---
7475	---	577	579	468	490	522	541	557	682
7671	196	568	574	465	487	519	535	552	671
7868	197	577	577	466	489	519	541	557	683
8064	196	570	575	466	489	521	537	554	673
8262	198	572	574	465	486	516	540	556	684
8458	196	572	577	467	490	521	539	555	678
8654	196	568	572	464	485	516	536	552	677
8850	196	574	577	467	490	521	539	555	679
9046	196	567	571	465	486	516	535	551	672
9243	197	577	578	468	490	521	540	557	683
9438	195	572	575	467	489	520	537	556	678
[b]9467	---	---	---	---	---	---	---	---	---
Average	196.3	572	575	466	488	519	538	555	679

[a]Start of 100-milliliter flow.

[b]End of 100-milliliter flow.

TABLE III. - CALCULATED EFFECT OF α AND β ON

EXPERIMENTALLY MEASURABLE PARAMETERS

Measurable parameter	Expression for dry sample	Expression for wet sample	$\alpha = 1$, $\beta = 1$ Dry = wet	$\alpha = 1$, $\beta = 0$		$\alpha = 0.9$, $\beta = 0.8$	
				Dry	Wet	Dry	Wet
			Mole fraction, number of moles of non-condensible gas per mole of methanol				
H_2	$\frac{2\alpha + \beta}{3\alpha + \beta}$	$\frac{2\alpha + \beta}{2 + 2\alpha}$	0.75	0.67	0.50	0.74	0.68
CO	$\frac{\alpha - \beta}{3\alpha + \beta}$	$\frac{\alpha - \beta}{2 + 2\alpha}$	0	.33	.25	.03	.03
CO_2	$\frac{\beta}{3\alpha + \beta}$	$\frac{\beta}{2 + 2\alpha}$	.25	0	0	.22	.21
CH_3OH	------	$\frac{1 - \alpha}{2 + 2\alpha}$	0	0	0	0	.03
H_2O	------	$\frac{1 - \beta}{2 + 2\alpha}$	0	0	.25	0	.05
Amount of noncondensible gas per mole of CH_3OH, liters			90	67		78	
Amount of condensate per 100 milliliters of feedstock, milliliters			0	32		~13	
Amount of H_2 per mole of CH_3OH, liters			67.5	44.9	33.5	57.7	53

TABLE IV. - CALCULATED EXPERIMENTAL DATA

Run	$4\frac{V_{100}}{V_{max}} = 3\alpha + \beta$	Fraction of methanol converted, α (from eq. (8))	Fraction of water consumed, β (eq. (13))	From gas analysis	From eq. (14)	CH_3OH content, wt %	Volume, milliliters	Pseudo-equilibrium rate constant for shift reaction, k_{eq}	Energy enrichment, $E_R = E_{out}/E_{in}$
				Mole fraction, x_{CO_2}		Amount of condensate calculated for 100 milliliters of feed			
Furnace temperature, T_F, 630 K (675° F)									
1	3.821	1.0	0.821	0.214	0.215	0	5.7	79	1.148
2	3.871	1.0	.871	.226	.225	0	4.1	153	1.144
3	3.836	.982	.890	.234	.232	4.6	4.6	258	1.140
4	3.745	.952	.888	.238	.237	43.2	6.8	349	1.134
5	3.646	.922	.881	.241	.242	53.8	9.0	502	1.128
6	3.522	.887	.860	.243	.244	58.9	12.1	507	1.122
7	3.393	.830	.830	.245	.245	60.4	15.3	522	1.118
8	3.196	.804	.783	.246	.245	61.7	20.2	452	1.111
Furnace temperature, T_F, 653 K (715° F)									
1	3.834	1.0	0.834	0.220	0.218	0	5.3	93	1.147
2	3.846	.996	.857	.226	.223	4.7	4.8	133	1.144
3	3.791	.975	.867	.232	.229	25.1	5.9	182	1.140
4	3.715	.949	.867	.236	.233	40.5	7.6	223	1.134
5	3.619	.919	.861	.239	.238	50.9	9.9	273	1.129
6	3.488	.882	.844	.243	.242	57.4	12.9	338	1.122
7	3.382	.852	.826	.245	.244	60.2	15.6	355	1.118
Furnace temperature, T_F, 680 K (765° F)									
1	3.715	0.990	0.744	0.203	0.200	----	----	---	-----
2	3.781	1.0	.781	.210	.210	0	7.0	43	1.150
3	3.801	1.0	.801	.217	.211	0	6.3	56	1.149
4	3.793	.986	.835	.220	.220	13.1	6.2	76	1.144
5	3.791	.982	.845	.223	.223	17.1	6.1	89	1.142
6	3.778	.970	.868	.229	.230	28.8	6.2	130	1.139
7	3.735	.950	.884	.236	.237	43.4	7.0	192	1.133
8	3.652	.923	.883	.240	.242	53.9	8.9	239	1.128
9	3.566	.899	.870	.244	.244	58.0	11.0	260	1.124
10	3.491	.879	.855	.246	.245	59.7	12.8	257	1.121

TABLE V. - TEMPERATURE DATA

(a) SI units

Run	Feedstock flow rate, milliliters/hr	Thermocouple location								
		Inlet	Outlet	Center of catalyst bed			Skin		Centerline		Temperature difference, ΔT
				Distance from start of bed, cm							
				2.54	7.62	12.7	4.57	11.43	4.57	11.43	4.57
		Thermocouple designation									
		T_1	T_2	T_3	T_4	T_5	T_6	T_7	T_6	T_7	----
		Temperature, K									
Furnace temperature, T_F, 630 K											
1	96.7	588	507	559	595	616	577	602	529	588	48
2	116.2	583	491	534	575	607	565	588	509	565	56
3	135.7	576	479	513	554	595	552	574	492	543	60
4	154.3	574	471	497	534	583	542	561	479	524	63
5	172.5	572	466	488	519	575	538	555	474	511	64
6	189.7	572	462	481	507	568	534	547	469	499	65
7	208.1	573	460	476	498	562	551	542	466	491	65
8	235.1	575	457	470	489	553	528	535	462	483	64
Furnace temperature, T_F, 653 K											
1	135.5	619	509	563	612	647	596	627	531	600	65
2	152.7	612	496	538	588	633	582	609	512	575	70
3	171.7	610	488	522	567	621	573	596	501	554	72
4	189.6	606	482	509	549	610	565	585	492	536	73
5	210.6	606	478	501	534	602	560	577	487	524	73
6	236.2	607	474	492	519	591	555	569	481	510	74
7	258.4	609	471	486	509	583	552	562	477	502	75
Furnace temperature, T_F, 680 K											
1	134.5	668	545	625	676	706	647	685	581	667	66
2	152.3	655	526	591	650	691	628	664	553	636	75
3	170.8	651	515	569	629	680	616	651	536	613	80
4	180.0	650	512	562	620	674	614	646	531	605	83
5	187.9	646	508	554	612	670	608	639	526	597	86
6	208.6	646	501	537	591	658	598	626	512	576	86
7	231.2	646	495	524	570	646	592	615	504	557	88
8	255.9	647	492	514	553	635	587	605	500	540	87
9	278.6	649	490	508	540	626	584	599	497	529	87
10	297.3	651	489	504	532	620	582	594	494	522	88

TABLE V. - Concluded.

(b) U.S. customary units

Run	Feedstock flow rate, milliliters/hr	Thermocouple location									
		Inlet	Outlet	Center of catalyst bed			Skin		Centerline		Temperature difference, ΔT
				Distance from start of bed, cm							
				1	3	5	1.8	4.5	1.8	4.5	1.8
		Thermocouple designation									
		T_1	T_2	T_3	T_4	T_5	T_6	T_7	T_6	T_7	----
		Temperature, °F									
Furnace temperature, T_F, 675° F											
1	96.7	582	537	566	586	598	576	590	549	582	26.7
2	116.2	579	552	552	575	593	569	582	538	569	31.1
3	135.7	575	522	540	563	586	562	579	529	557	33.3
4	154.3	574	517	532	552	579	557	567	522	547	35.0
5	172.5	573	514	527	544	575	554	565	519	539	35.5
6	189.7	573	512	523	537	571	552	559	516	533	36.1
7	208.1	574	511	520	532	568	550	557	514	528	36.1
8	235.1	575	509	517	527	563	549	553	512	524	36.7
Furnace temperature, T_F, 715° F											
1	135.5	599	538	568	595	615	587	604	550	589	36.1
2	152.7	595	531	554	582	607	579	594	540	575	38.9
3	171.7	594	527	545	570	600	574	587	534	563	40.0
4	189.6	592	523	538	560	594	569	580	529	553	40.5
5	210.6	592	521	534	552	590	567	576	526	547	40.5
6	236.2	593	519	529	544	584	564	572	523	539	41.2
7	258.4	594	517	525	538	579	562	568	520	534	41.7
Furnace temperature, T_F, 765° F											
1	134.5	627	558	603	631	648	615	636	578	626	36.7
2	152.3	619	548	584	617	639	604	624	563	609	41.7
3	170.8	617	542	572	605	633	598	617	553	596	44.4
4	180.0	617	540	568	600	630	597	614	550	592	46.1
5	187.9	614	538	563	595	628	593	610	548	587	45.6
6	208.6	614	534	554	584	621	588	603	540	575	47.7
7	231.2	614	530	547	572	614	584	597	535	565	48.9
8	255.9	615	529	541	563	608	582	592	533	555	48.3
9	278.6	616	528	538	555	603	580	588	531	549	48.4
10	297.3	617	527	535	551	600	579	585	530	545	48.9

TABLE VI. - LEAST-SQUARES FIT TO EQUATION $Sv = A \exp\left(-\frac{\omega}{T_4}\right)$

Fraction of methanol converted, α	Inverse temperature, $1/T_4$, K^{-1}	Hydrogen				Methanol			
		Space velocity, Sv, hr^{-1}	$-\omega$, K	A, hr^{-1}	Correlation coefficient	Space velocity, Sv, hr^{-1}	ω, K	A, hr^{-1}	Correlation coefficient
0.92	1.840×10^{-3} 1.811 1.781	2010 2430 2970	6618	0.3901	1.000	743 910 1110	6803	0.2032	0.9999
0.90	1.854×10^{-3} 1.826 1.799	2100 2540 3130	7253	1.448	0.9993	791 965 1190	7424	0.7486	0.9997
0.89	1.860×10^{-3} 1.833 1.808	2130 2590 3200	7820	4.394	0.9990	812 995 1230	7980	2.259	0.9994
0.88	1.866×10^{-3} 1.842 1.816	2170 2645 3280	8263	10.77	1.000	835 1025 1270	8385	5.215	1.000
0.87	1.872×10^{-3} 1.847 1.822	2205 2695 3350	8364	13.89	0.9973	860 1055 1305	8341	5.185	0.9999

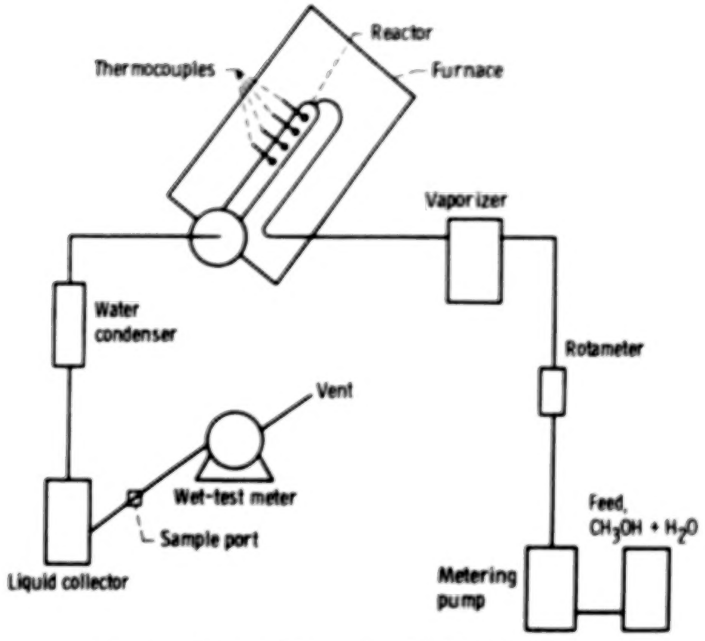


Figure 1. - Apparatus for converting methanol to hydrogen.

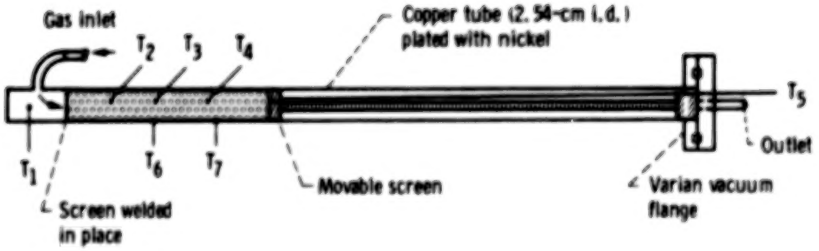


Figure 2. - Methanol reactor, where thermocouples T_1 to T_5 measure gas temperature and thermocouples T_6 and T_7 measure skin temperature.

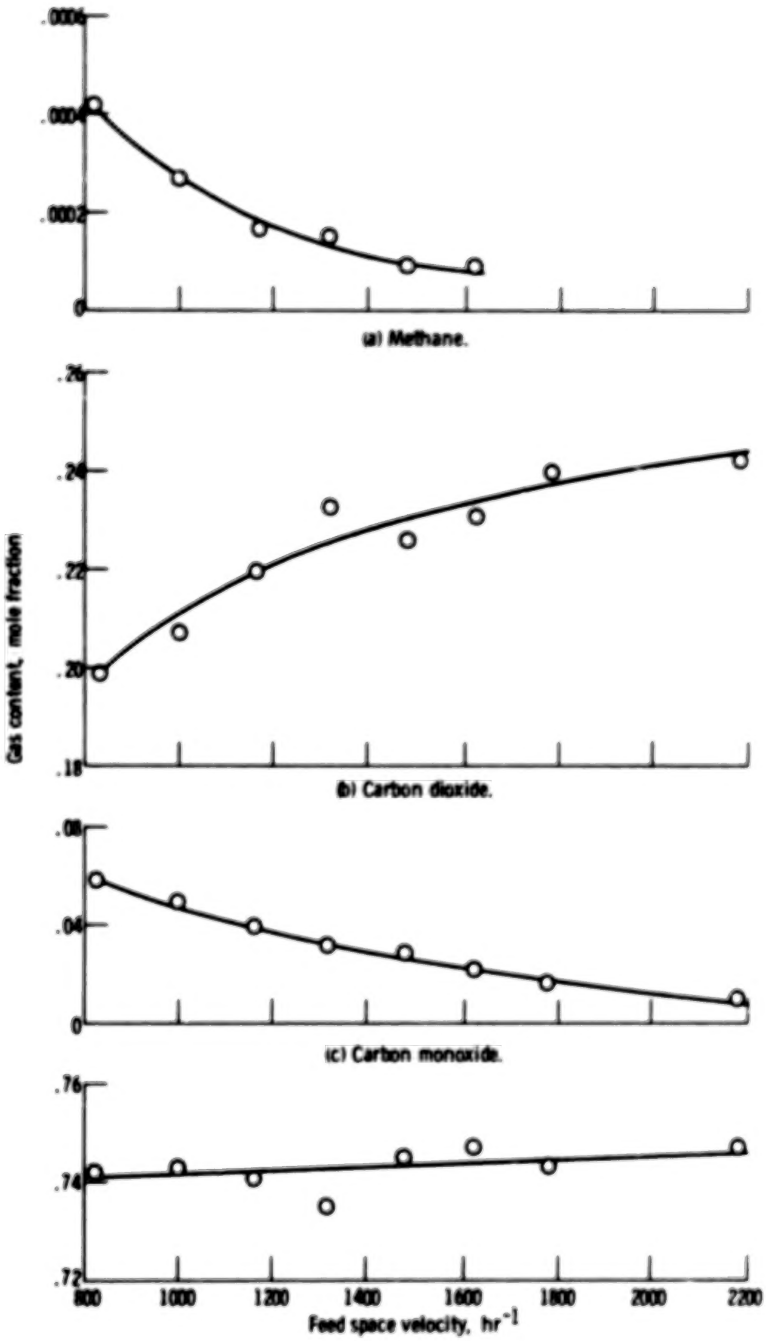


Figure 3. - Gas chromatograph analysis of reactor exhaust gases as function of feed space velocity for furnace temperature of 653 K (719° F).

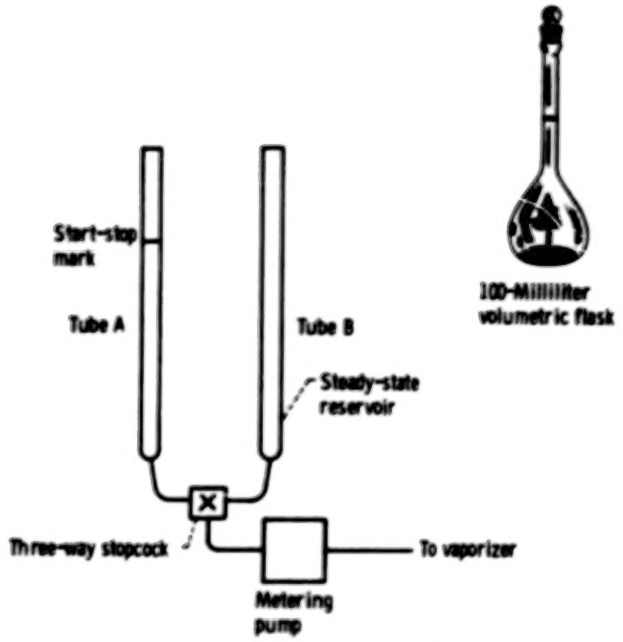


Figure 4. - Feed metering setup.

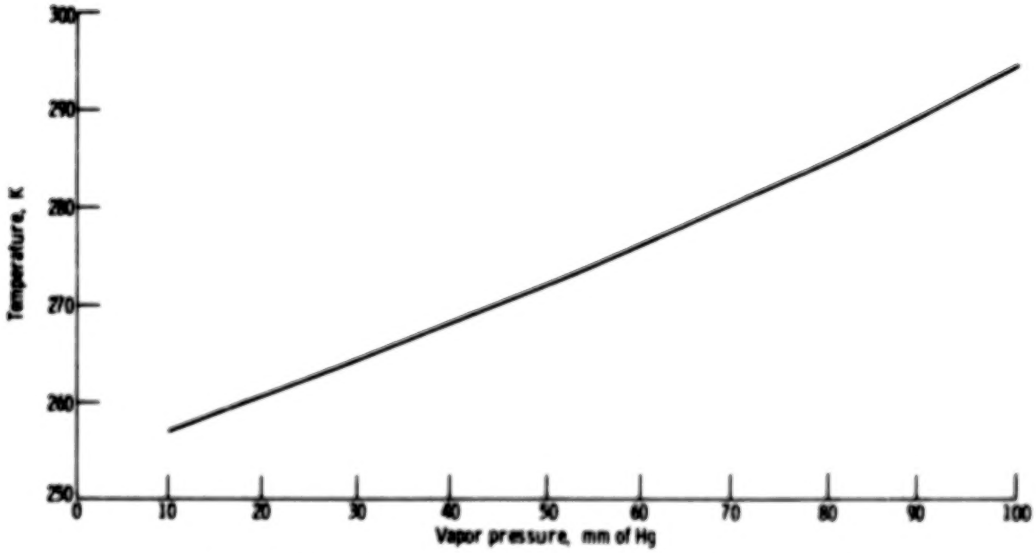


Figure 5. - Methanol vapor pressure as a function of temperature. (From ref. 9.)

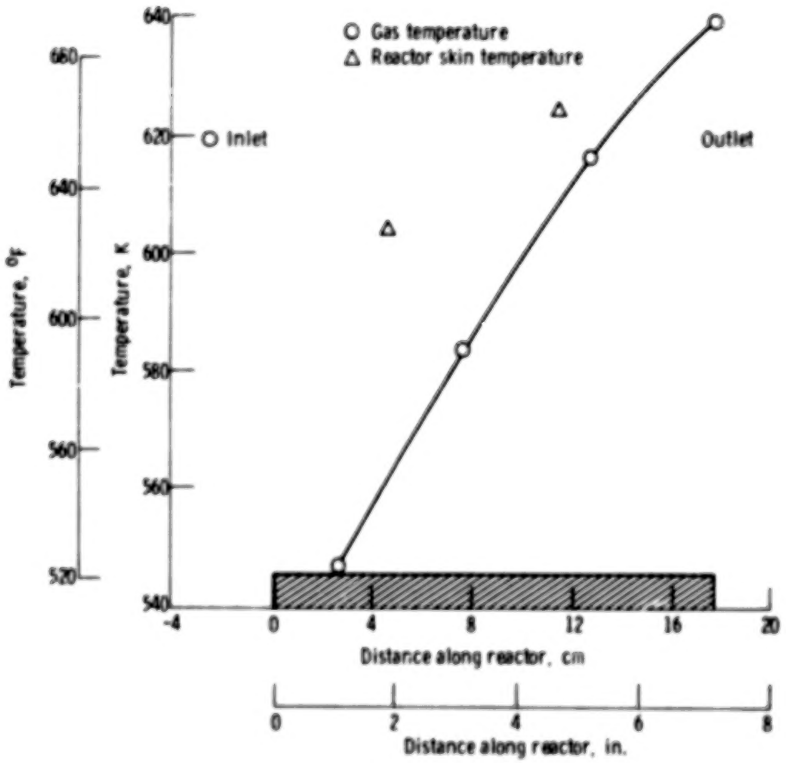


Figure 6. - Typical reactor temperature profile.

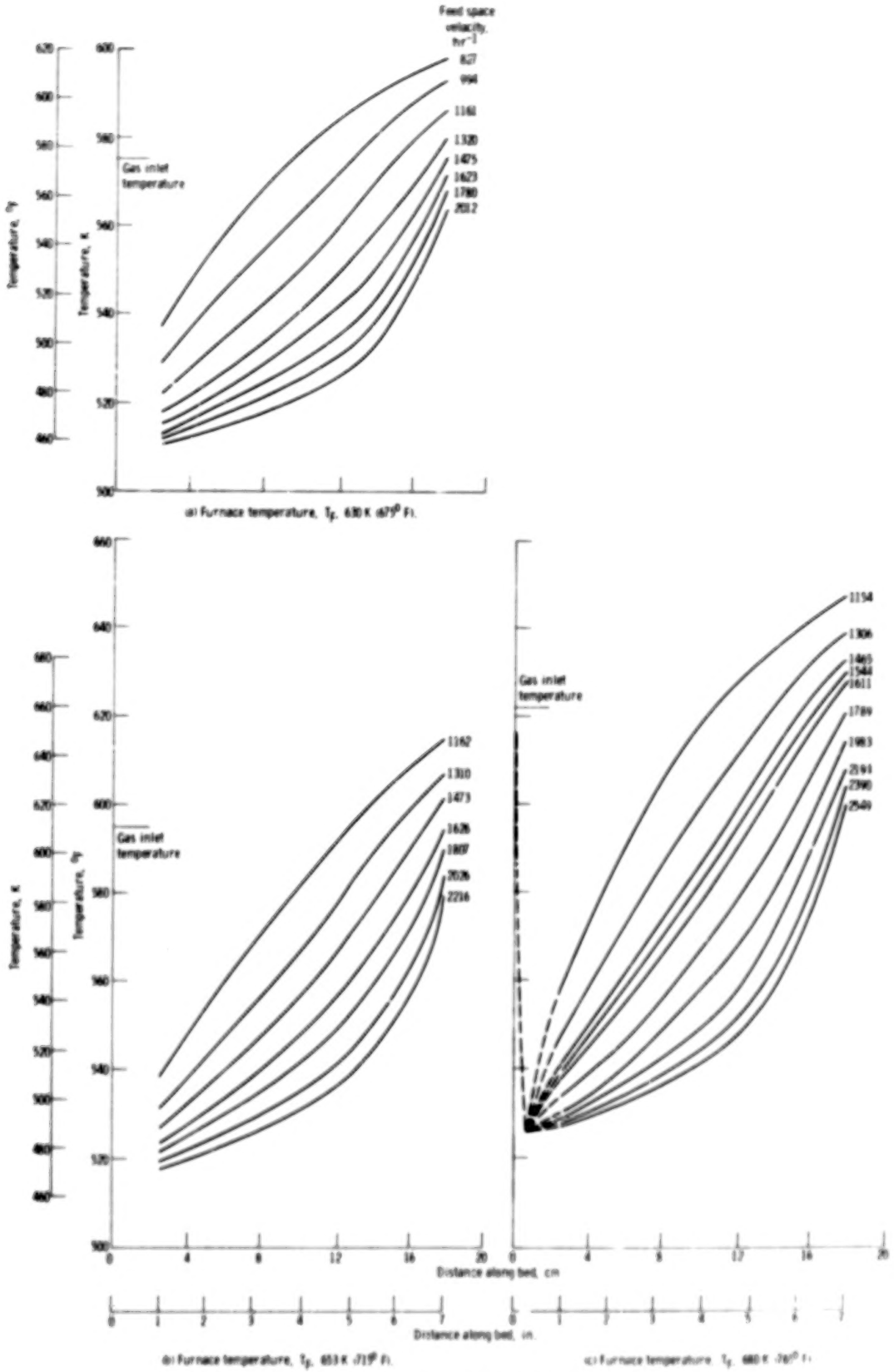


Figure 7. - Reactor temperature profile for various feed space velocities.

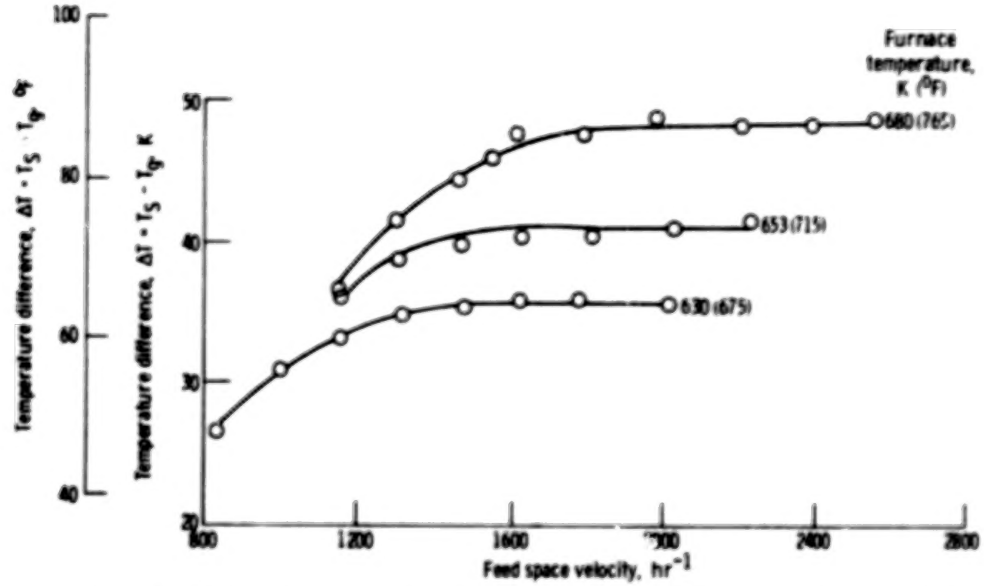

Temperature difference, ΔT = T_S - T_gr °F
Temperature difference, ΔT = T_S - T_gr K
Furnace temperature, K (°F)
680 (765)
653 (715)
630 (675)
Feed space velocity, hr⁻¹

Figure 8. - Difference between reactor skin and gas temperatures 4.57 centimeters along reactor as a function of feed space velocity and furnace temperature.

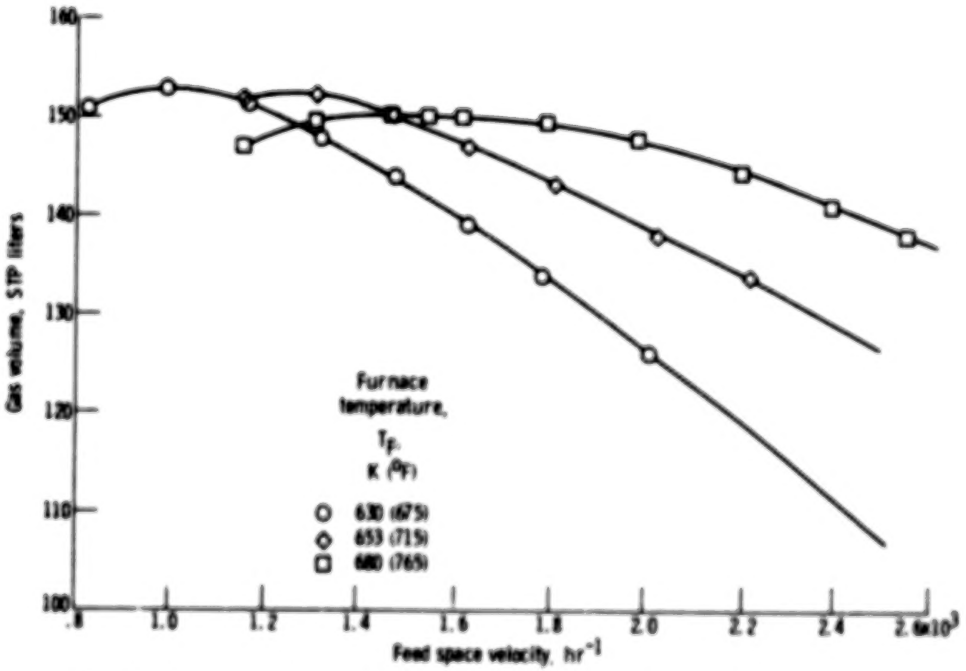


Figure 9. - Volume of gas obtained from 100 milliliters of feed as a function of feed space velocity and furnace temperature.

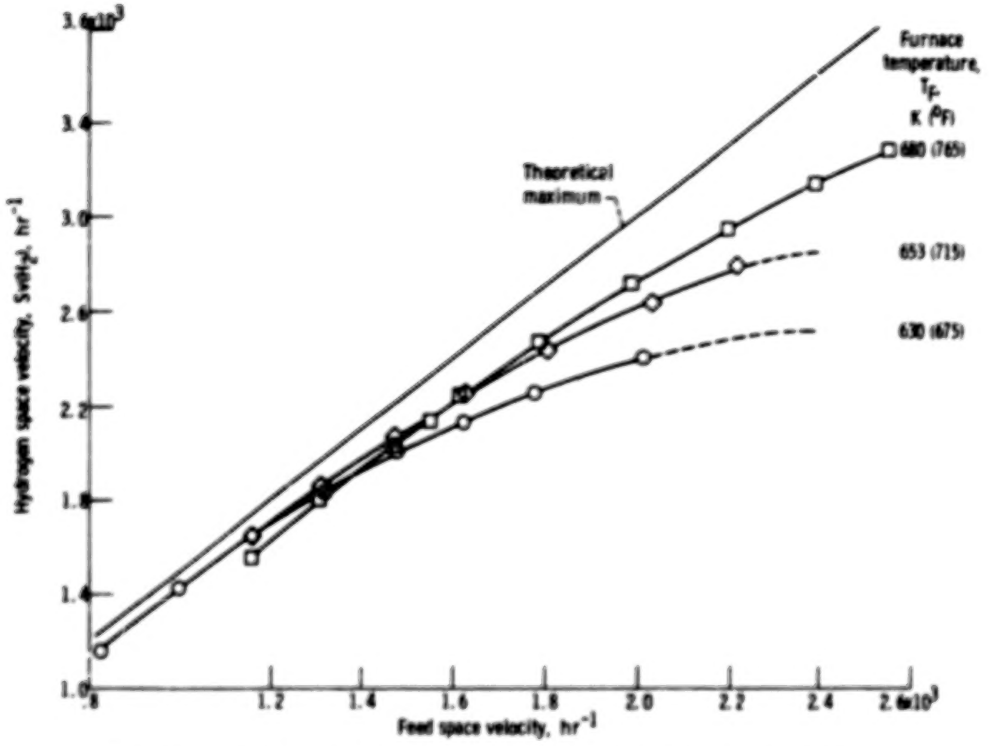


Figure 10. - Hydrogen space velocity as a function of feed space velocity and furnace temperature.

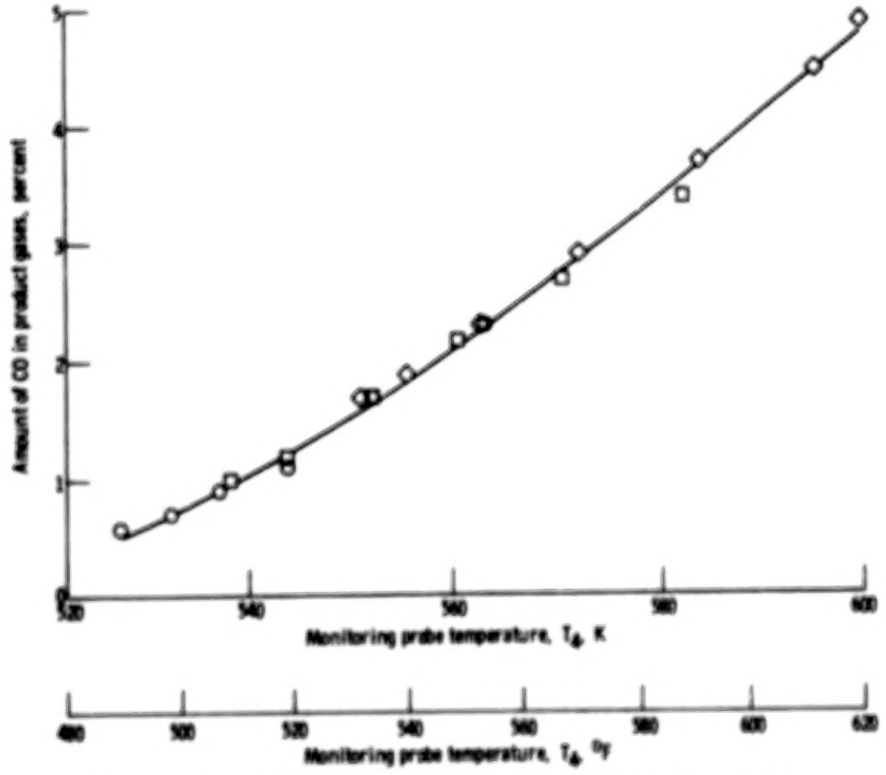


Figure 11. - Amount of carbon monoxide in product gases as a function of monitoring probe temperature.

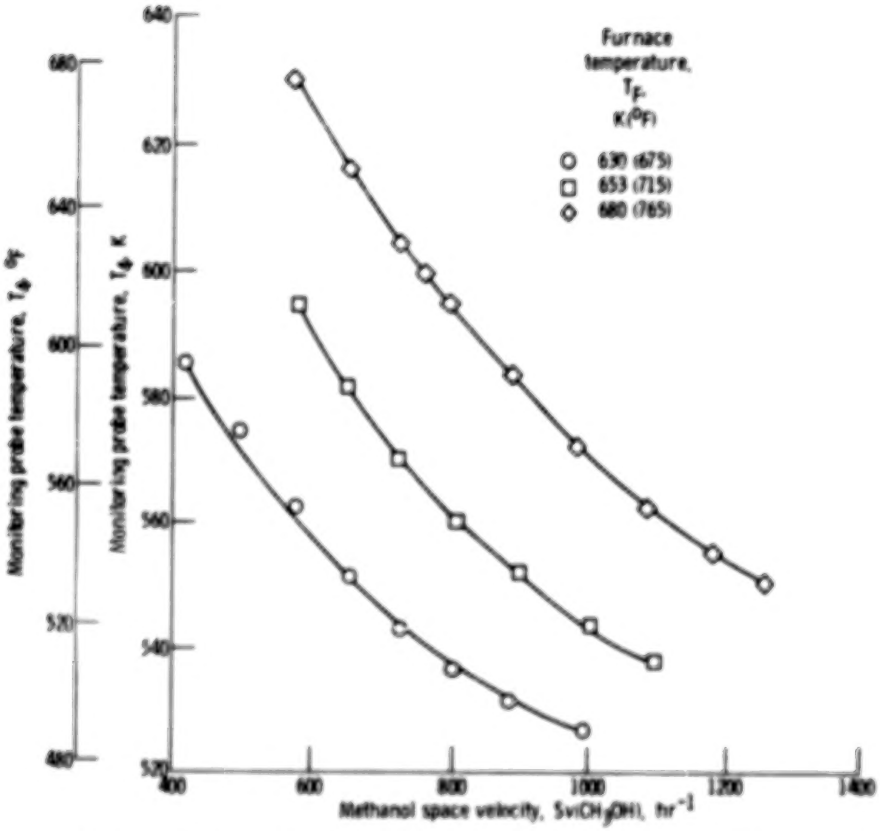


Figure 12. - Monitoring probe temperature as function of methanol space velocity and furnace temperature.

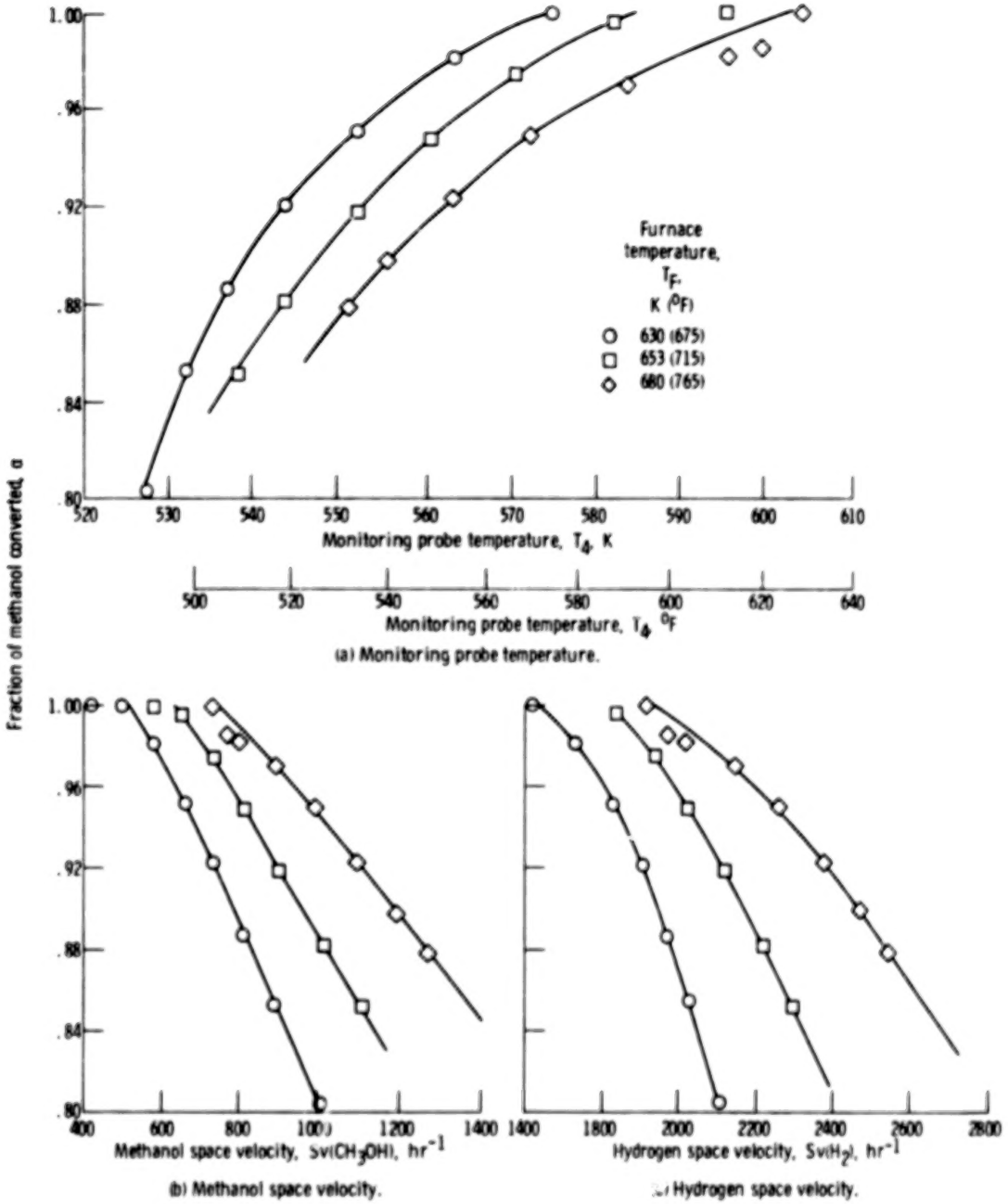
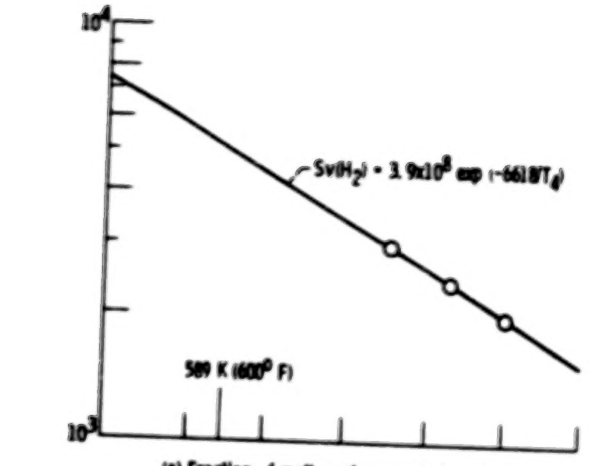
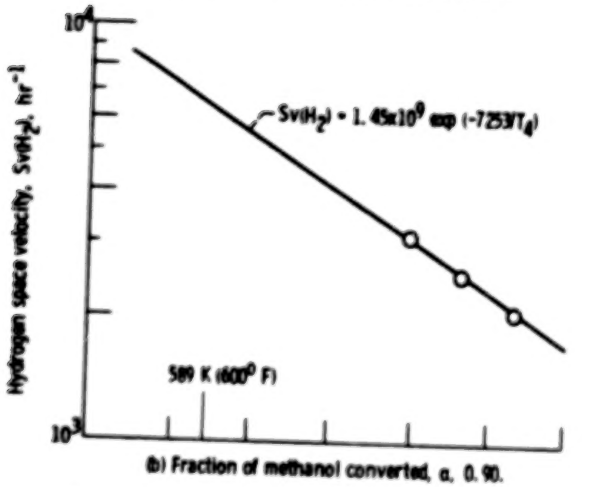


Figure 13. - Monitoring probe temperature and methanol and hydrogen space velocities as functions of fraction of methanol converted and furnace temperature.

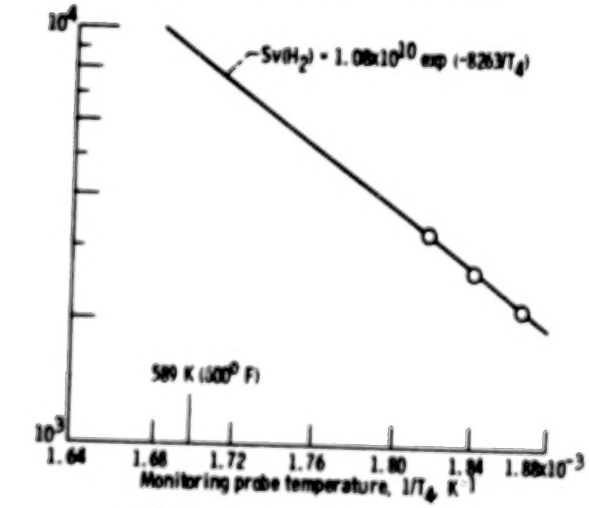


(a) Fraction of methanol converted, α, 0.92.



Hydrogen space velocity, $Sv(H_2)$, hr^{-1}

(b) Fraction of methanol converted, α, 0.90.



(c) Fraction of methanol converted, α, 0.88.

Figure 14. - Semilog plots of hydrogen space velocity as function of inverse monitoring probe temperature and fraction of methanol converted.

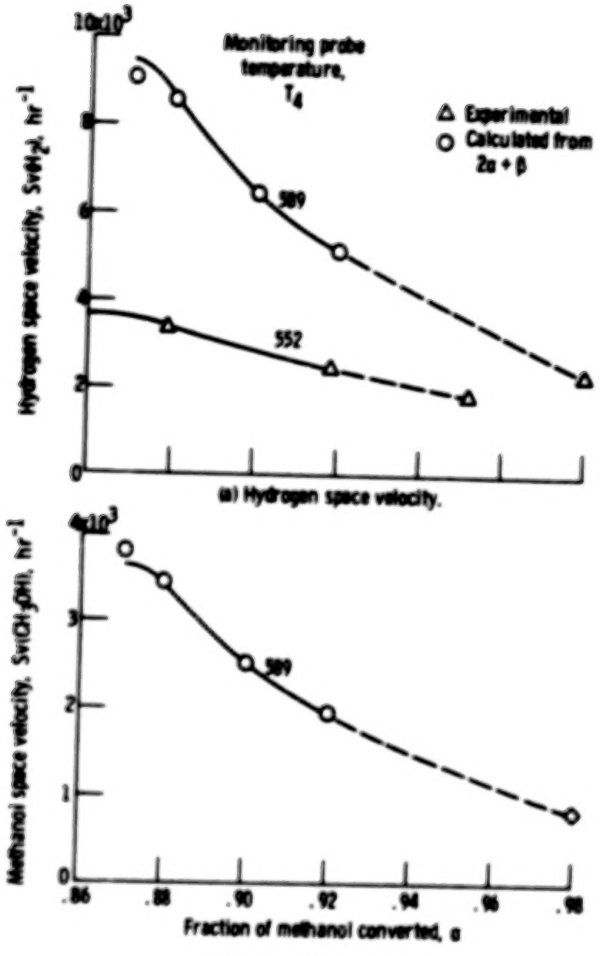


Figure 15. - Calculated hydrogen and methanol space velocities as a function of fraction of methanol converted.

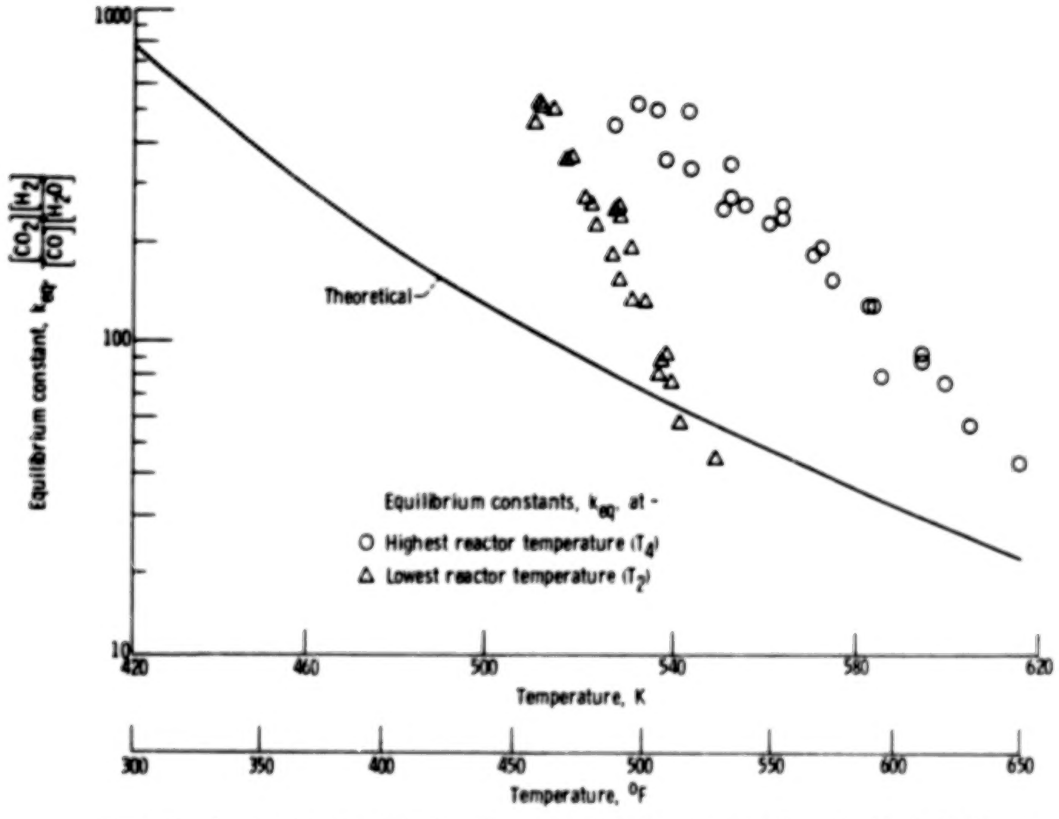


Figure 16. - Experimental and theoretical equilibrium constants for water-gas shift reaction $CO + H_2O \rightleftharpoons CO_2 + H_2$.

1. Report No. NASA TP-1247	2. Government Accession No.	3. Recipient's Catalog No.
4. Title and Subtitle **CATALYTIC DECOMPOSITION OF METHANOL FOR ONBOARD HYDROGEN GENERATION**		5. Report Date June 1978 6. Performing Organization Code
7. Author(s) **Theodore A. Brabbs**		8. Performing Organization Report No. E-9472
9. Performing Organization Name and Address **National Aeronautics and Space Administration** **Lewis Research Center** **Cleveland, Ohio 44135**		10. Work Unit No. 776-71 11. Contract or Grant No.
12. Sponsoring Agency Name and Address **National Aeronautics and Space Administration** **Washington, D.C. 20546**		13. Type of Report and Period Covered Technical Paper 14. Sponsoring Agency Code
15. Supplementary Notes		

16. Abstract

The steam reformation of an equimolar mixture of methanol and water on a copper chromite catalyst was studied at three furnace temperatures and at feed space velocities from 800 to 2600 per hour. The hydrogen space velocity could be related to the reactor temperature by the equation $Sv = A \exp(-\omega/T)$, where A and ω are constants determined for each value of α and T is temperature. At a methanol conversion of 0.87 and a reactor temperature of 589 K, the extrapolated value of the hydrogen space velocity was 9400 per hour. This velocity was used to estimate the size of an onboard hydrogen reactor for automotive applications. Such a reactor would need only about 0.8 liter of catalyst to produce 7630 STP liters (1.5 lb) of hydrogen per hour. This quantity of catalyst would fit into nine tubes 17.8 centimeters long and 2.54 centimeters in inside diameter, which is smaller than most mufflers. The reactor products would contain 12 to 13 percent more chemical energy than the incoming methanol and water.

17. Key Words (Suggested by Author(s))	18. Distribution Statement
Hydrogen generator **Methanol reformation** **Methanol decomposition** **Onboard hydrogen generation**	**Unclassified - unlimited** **STAR Category 28**

19. Security Classif. (of this report)	20. Security Classif. (of this page)	21. No. of Pages	22. Price*
Unclassified	**Unclassified**	**45**	**A03**

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NASA-Langley, 1978